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2,4-Bis(α,α-dimethylbenzyl)phenol

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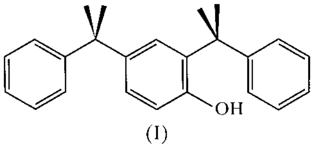
The structure of the title compound, 2,4-bis(1-methyl-1-phenylethyl)phenol, $C_{24}H_{26}O$, was found to have a torsion angle of 129.95 (13)° for the C—C bond that connects the benzyl carbon to the phenol ring *ortho* to the OH group. A value of ~50° was expected from molecular mechanics calculations. Intermolecular interactions, in particular O—H···O and edge–face π bonding, may contribute to this discrepancy. Intramolecular O—H···π bonding is also observed.

Comment

As part of our investigation into the extraction of caesium by 2-benzylphenol and its derivatives (Bryan *et al.*, 1999; Delmau *et al.*, 2000), we wished to examine the structural effects of alkyl substitution on the benzyl C atom. Molecular mechanics (MM) calculations suggest that metal-ion selectivity may be affected by the rotational potential energy surface for the C—C bond that connects the benzyl carbon to the phenol ring *ortho* to the OH group (Delmau *et al.*, 2000). In other words, the value for this torsion angle (C3—C2—C7—C11, referred to here as ψ) varies in MM minimizations depending on the alkali metal ion complexed, from 100° for Cs^+ to 126° for Li^+ (Bryan *et al.*, 1999). Varying the steric environment at the *ortho* benzyl C atom will affect the potential energy surface, and therefore also affect selectivity.

We reported previously the structure of 2-benzylphenol, which exhibited a ψ value of 11.1 (2)°. This unusually low value was attributed to intermolecular O—H···O hydrogen bonding and edge-to-face arene interactions (Bryan *et al.*, 1999), and to the relatively low conformational energies calculated for 2-benzylphenol by MM at low ψ (Delmau *et al.*, 2000). The only published structure of a 2-benzylphenol derivative containing alkyl substitution at the benzyl carbon is 2,4,6-tris(α,α-dimethylbenzyl)phenol, which exhibits ψ values of 122.3 (3) and −124.4 (3)° for the two benzyl groups *ortho* to the hydroxyl group (Kurashev *et al.*, 1986). We sought to investigate the structure of the title compound, (I), because of its commercial availability and because MM calculations predicted a minimum conformational energy for ψ of ~50° for methyl substitution on the benzyl carbon [2-(α-methylbenzyl)phenol; Delmau *et al.*, 2000].



(I)

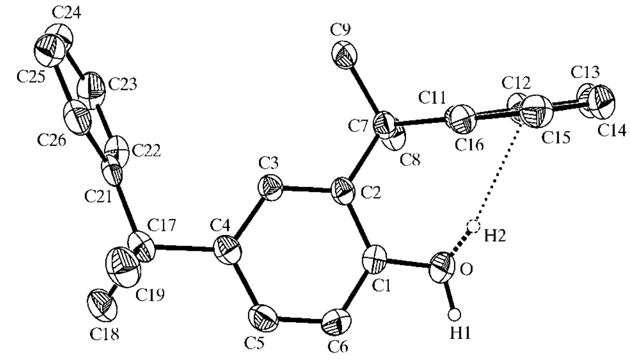


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

The structure of (I) (Fig. 1) is dramatically different from 2-benzylphenol (Bryan *et al.*, 1999), but is quite similar to the more closely related 2,4,6-tris(α,α-dimethylbenzyl)phenol (Kurashev *et al.*, 1986). Specifically, the ψ angle (C3—C2—C7—C11) is 129.95 (13)° in (I), almost identical to the values

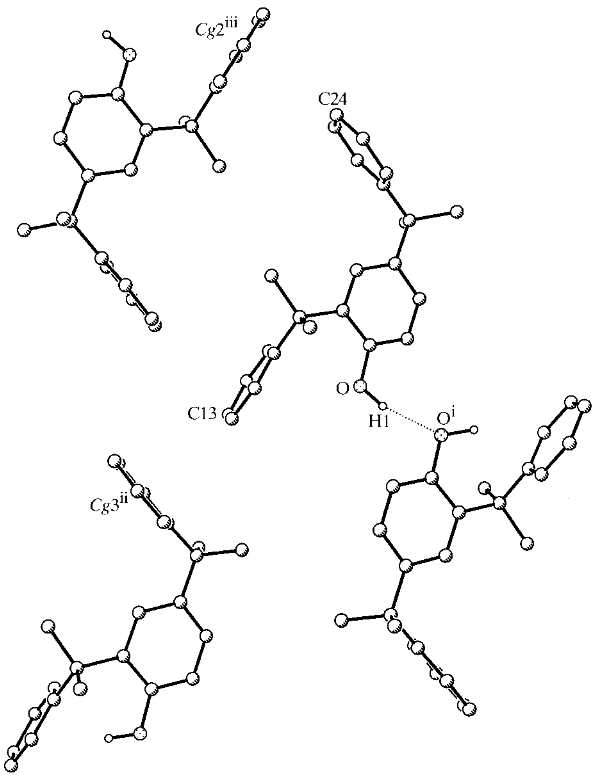


Figure 2
Packing diagram illustrating the edge–face π and O—H···O interactions of (I). For clarity, all atoms are represented as circles. All H atoms, except those of hydroxy, have been omitted [symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x-1, y-1, z$; (iii) $1-x, 1-y, -z$]. *Cg*2 and *Cg*3 represent the centroids of rings C11–C16 and C21–C26, respectively.

reported for 2,4,6-tris(α,α-dimethylbenzyl)phenol. These results suggest that the MM calculations performed for 2-(α-methylbenzyl)phenol do not correlate well to structures determined containing the 2-(α,α-dimethylbenzyl)phenol fragment, possibly due to intermolecular forces in the crystal structure.

The hydroxyl H atom in (I) was determined to be disordered over two sites (50:50) by examination of an electron-density difference map. One position (H1) is oriented outwards from the molecule, and forms an intermolecular hydrogen bond to O^{i} [symmetry code: (i) $-x, 1-y, 1-z$]. The other location (H2) is oriented inwards, forming an O—H$\cdots\pi$ interaction (Steiner *et al.*, 1996; Bakshi *et al.*, 1994) with the phenyl group (Table 2).

The three arene rings in this structure are each planar within 0.016 Å, and are all roughly orthogonal to each other. The interarene angles are *Cg*1–*Cg*2 = 80.36 (7), *Cg*1–*Cg*3 = 71.43 (8), and *Cg*2–*Cg*3 = 71.88 (8)°, where *Cg*1 = C1–C6, *Cg*2 = C11–C16 and *Cg*3 = C21–C26 (Table 2). No π–π ring stacking is observed, but two edge–face arene interactions are detected, which are illustrated in Fig. 2. These interactions are further quantified in Table 2, where metrical parameters for the two C—H$\cdots\pi$-centroid interactions are listed. Taken together, the hydrogen bonds of the hydroxyl group and the edge–face interactions of the arene groups, a three-dimensional network is formed.

Experimental

The title compound was obtained from a commercial source (Aldrich) and was recrystallized from 2,2,2-trifluoroethanol.

Crystal data

$C_{24}H_{26}O$
$M_r = 330.4$
Triclinic, $P\overline{1}$
$a = 6.1716$ (9) Å
$b = 11.7924$ (14) Å
$c = 13.2197$ (14) Å
$\alpha = 97.731$ (10)°
$\beta = 97.109$ (12)°
$\gamma = 97.353$ (12)°
$V = 935.7$ (2) Å^3

$Z = 2$
$D_x = 1.17$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–17.6°
$\mu = 0.07$ mm^{-1}
$T = 173$ K
Plate, colourless
0.71 × 0.47 × 0.13 mm

Data collection

Nonius CAD-4 diffractometer
ω scans
3458 measured reflections
3282 independent reflections
2656 reflections with $I > 2\sigma I$
$R_{\rm int} = 0.028$
$\theta_{\max} = 25.0°$

$h = -7 \to 7$
$k = -14 \to 0$
$l = -15 \to 15$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Table 1
Selected geometric parameters (Å, °).

O—C1	1.3809 (18)		
C1—O—H1	115 (3)	O—C1—C6	117.94 (13)
C1—O—H2	110 (2)	O—C1—C2	121.30 (13)
C3—C2—C7—C11	129.95 (13)	C2—C7—C11—C16	−50.85 (16)
C1—C2—C7—C11	−53.15 (16)	C2—C7—C11—C12	130.81 (14)
C3—C4—C17—C21	14.92 (18)	C4—C17—C21—C26	−114.81 (15)
C5—C4—C17—C21	−167.81 (13)	C4—C17—C21—C22	65.71 (17)

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.110$
$S = 1.07$
3282 reflections
236 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2606P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O—H1$\cdots$O^{i}	0.95 (4)	2.05 (4)	2.944 (2)	156 (4)
O—H2$\cdots$*Cg*2	1.02 (4)	2.56	3.54	162
C13—H13$\cdots$*Cg*3^{ii}	0.95	2.83	3.61	141
C24—H24$\cdots$*Cg*2^{iii}	0.95	2.74	3.57	146

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x-1, y-1, z$; (iii) $1-x, 1-y, -z$.

A 1.1 mm collimator was used. All C-bound H atoms were placed in calculated positions, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 (CH) or 1.5 (CH_3) times the equivalent isotropic displacement parameter of the atom to which they were attached. The C—H distances used depend on the type of C atom: $C_{\rm aromatic}$—H = 0.95 and $C_{\rm methyl}$—H = 0.98 Å. Methyl H atoms were allowed to rotate about the adjacent C—C bond. The hydroxyl H atom was found to be disordered over two sites (50:50). The positional parameters of the hydroxyl H atom were allowed to refine and $U_{\rm iso}$(H) was set at $1.5U_{\rm eq}$(O).

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1993); cell refinement: *CAD*-4-*PC*; data reduction: *XCAD*4 (Harms, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *PLATON* (Spek, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1283). Services for accessing these data are described at the back of the journal.

References

Bakshi, P. K., Linden, A., Vincent, B. R., Roe, S. P., Adhikesavalu, D., Cameron, T. S. & Knop, O. (1994). *Can. J. Chem.* **72**, 1273–1293.

Bryan, J. C., Delmau, L. H., Hay, B. P., Nicholas, J. B., Rogers, L. M., Rogers, R. D. & Moyer, B. A. (1999). *Struct. Chem.* **10**, 187–203.

Delmau, L. H., Bryan, J. C., Engle, N. L., Sachleben, R. A., Moyer, B. A. & Hay, B. P. (2000). *Calixarene Molecules for Separations*, edited by G. J. Lumetta & R. D. Rogers. Washington, DC: American Chemical Society. In the press.

Enraf–Nonius (1993). *CAD*-4-*PC*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.

Harms, K. (1995). *XCAD*4. University of Marburg, Germany.

Kurashev, M. V., Struchkov, Yu. T., Veretyakhina, T. G. & Shklover, V. E. (1986). *Izv. Akad. Nauk SSSR Ser. Khim.* p. 1843.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1994). *SHELXTL*. Version 5.03/IRIX. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1999). *PLATON*. University of Utrecht, The Netherlands.

Steiner, T., Starikov, E. B. & Tamm, M. (1996). *J. Chem. Soc. Perkin Trans.* **2**, 67–71.